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A Statistical Derivation of the Average Degree of Polymerization in a Stirred Tank Reactor

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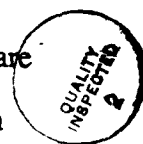
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Abstract

The statistical approach in its many forms has been a powerful tool in describing the structural evolution of nonlinear polymers, but has been limited in its application to batch processes. This restriction is removed by considering the paradigm of A_f homopolymerization in a homogeneous stirred tank reactor. The number- and weight-average degrees of polymerization are derived from recursive arguments which properly account for the non-random combination of monomers caused by the residence time distribution. The results are in agreement with those derived from the kinetic equations. This route is not necessarily a simpler or more powerful approach than solution of the kinetic equations, but it does provide new insights into this particular problem, as well as demonstrating the versatility of the statistical approach.



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Introduction

Stepwise polymers produced in a homogeneous continuous stirred tank reactor¹ (HCSTR) can exhibit significantly broader distributions than their counterparts produced in batch reactors. The homopolymerization of A_2 monomers serves to illustrate this. In a batch reactor the molecular weight distribution is the most probable (or geometric) distribution:¹

$$P_n = p^{n-1} (1-p) \quad (1)$$

where P_n is the molar fraction of n -mers, and p is the extent of reaction (the probability that a functional group has reacted). This distribution gives the following number- and weight-average degrees of polymerization:

$$DP_n = \frac{1}{1-p} \quad (2)$$

$$DP_w = \frac{1+p}{1-p} \quad (3)$$

The polydispersity of the polymer thus has an upper bound of two. The conversion is related to time t through the Damköhler number Da by the following relationship:

$$p = \frac{Da}{1 + Da} \quad (4)$$

where $Da = kfc_{10}$, k is the rate constant for functional group (not monomer) reaction, f is the functionality of the monomer (here 2), and c_{10} is the initial monomer concentration.

In an HCSTR, on the other hand, the distribution takes a more complicated form:¹

$$P_n = \frac{(2n-2)!}{n!(n-1)!} \frac{p^{n-1}}{(1+p)^{2n-1}} \quad (5)$$

which yields the following average degrees of polymerization:

$$DP_n = \frac{1}{1-p} \quad (6)$$

$$DP_w = \frac{1+p^2}{(1-p)^2} \quad (7)$$

Here, in contrast to the previous case, the polydispersity has no upper bound. The conversion is related to the relative rates of exit and reaction through the Damköhler number by the following relation:

$$p = 1 - \frac{\sqrt{1 + 4Da} - 1}{2Da} \quad (8)$$

where $Da = k\theta c_{10}$, c_{10} is the entering monomer concentration, and the mean residence time θ is the ratio of the volume of the reactor to the volumetric throughput rate.

Since for linear polymerizations broad distributions are easily obtained in an HCSTR, for nonlinear polymerizations one might expect the situation to be even more severe, such that the gel point could be advanced considerably. Several researchers have investigated the behavior of nonlinear polymerizations in HCSTRs. With regard to step polymerizations, the first work is that of Cozewith et al.,² which solved both the steady state and start-up problems for A_{∞} homopolymerization. For finite functionality systems, Gupta and coworkers³⁻⁵ have analyzed HCSTRs in series, the effect of oscillations in feed, and the effects of intramolecular reaction. Hendriks and Ziff⁶ have analyzed the problem starting with the Smoluchowski coagulation equation, and have looked at different coagulation kernels, analyzing both A_2 and

A_{∞} homopolymerization (which describes as well the critical behavior of the A_f system).

Nonlinear free-radical systems have also been studied.⁷⁻¹¹

Common to all of these analyses is the use of the kinetic equations describing polymerization. This approach would seem necessary because the various statistical methods, which are so useful for describing nonlinear polymerizations, have been held (usually implicitly) to be valid only for batch polymerizations.^{12,13} The non-geometric character of the distribution of eq 5 would thus seem to be beyond statistical reach, but yet Biesenberger and Tadmor justify it with combinatoric reasoning.^{1,14} Thus, this alleged restriction is not absolute. Nonetheless, the question must be asked: how are the ideality assumptions (equal reactivity and independent reaction) violated, so that simple application of statistical methods is invalid? Then, is there a correct statistical route to the average properties? The paradigm of random step homopolymerization of f -functional monomers, analyzed by the recursive method,¹⁵ serves to answer both questions, with the answer to the latter being "yes."

Statistical (Recursive) Derivation.

DP_w .

Consider the homopolymerization of f -functional monomers in an HCSTR operating at steady state, for which cyclization is prohibited, and for which only monomer enters the reactor. To derive the weight-average degree of polymerization, we first grab a (zeroth generation) monomer at random, so that we can write:

$$DP_w = 1 + f E(N_A^{out}) \quad (9)$$

where $E(N_A^{out})$ is the expected number of attached monomers looking out from a functional group.¹⁵ We must realize two things: (1) the probability of any of the f functional groups on

the monomer having reacted is dependent upon the residence time of that monomer, and (2) the only correlation between the states of the different functional groups is the fact that they all share the same residence time. These two points correspond to violations of the equal reactivity assumption and the independent reactivity assumption, respectively. The source of these nonidealities, however, is not intrinsic to the reaction chemistry, but rather to the reactor configuration.

As an HCSTR is perfectly mixed, the residence time distribution is described by an exponential distribution:

$$\rho(t)dt = \frac{1}{\theta} e^{-t/\theta} dt \quad (10)$$

Given a residence time t of the zeroth generation monomer (see Figure 1), the probability of a functional group having reacted is given by the following:

$$p(t) = 1 - e^{-t/\tau} \quad (11)$$

where τ is the time scale for reaction, equal to $[k(1-p)fc_{10}]^{-1}$, such that $\theta/\tau = Da(1-p)$. The overall conversion is thus given by:

$$p = \int_0^{\infty} p(t) \rho(t) dt = \frac{\theta}{\theta + \tau} = \frac{Da(1-p)}{1 + Da(1-p)} \quad (12)$$

which is consistent with eq 8.

Conditioning upon residence time, we can then write:

$$E(N_A^{out}) = \int_0^{\infty} E(N_A^{out} | t) \rho(t) dt \quad (13)$$

To evaluate $E(N_A^{\text{out}} | t)$, we must first condition upon the time t' at which the reaction occurred (see Figure 1):

$$E(N_A^{\text{out}} | t) = 1 - e^{-t/\tau} + (f-1) \int_0^t E(N_A^{\text{out}} | \text{one group reacted at time } t') \frac{1}{\tau} e^{-(t-t')/\tau} dt' \quad (14)$$

where the weighting function in the integrand is the probability density of reaction at time t' given a residence time t , which is consistent with eq 11. To close the recursion, we must further condition upon the residence time t'' of the first generation monomer (see Figure 1):

$$E(N_A^{\text{out}} | t) = 1 - e^{-t/\tau} + (f-1) \frac{1}{\tau} e^{-t/\tau} \int_0^t \int_0^\infty E(N_A^{\text{out}} | t'') \rho'(t''-t') dt'' e^{t'/\tau} dt' \quad (15)$$

The recursion thus does not close algebraically, as it does in the case of a batch reactor,¹⁵ but rather gives a double integral equation.

The distribution $\rho'(t''-t')$, which is the probability density that a monomer has a residence time t'' given that one of its groups reacted at t' , is a function only of $(t''-t')$ because the residence time distribution of a monomer, one group of which reacted at time t' , is insensitive to the fact that it must have remained in the reactor for a subsequent period t' . The distribution is given by the following:

$$\rho'(t) dt = \left(\frac{1}{\theta} + \frac{1}{\tau} \right) e^{-t/\tau} e^{-t/\theta} dt \quad (16)$$

i.e. simply the (properly normalized) product of the probabilities of a functional group escaping both reaction and exit.

The double integral equation can now be transformed to a second-order ordinary differential equation, and the result is:

$$E''(N_A^{\text{out}} | t) - \frac{1}{\theta} E'(N_A^{\text{out}} | t) + \frac{f-2}{\tau} \left(\frac{1}{\tau} + \frac{1}{\theta} \right) \left(E(N_A^{\text{out}} | t) + \frac{1}{f-2} \right) = 0 \quad (17)$$

The character of the solution will differ depending on whether $f=2$ or $f>2$; this is to be expected, since a linear system is very different from a nonlinear one. Before proceeding to the solutions, though, we can answer the first question posed in the Introduction.

If we had naively assumed, in eq 14, that the first generation monomer were also randomly chosen, we would have written that

$$E(N_A^{\text{out}} | \text{one group reacted at time } t') = E(N_A^{\text{out}}) \quad (18)$$

The recursion would thus have closed algebraically, and we would have obtained:

$$DP_w = \frac{1 + \int_0^{\infty} p(t) \rho(t) dt}{1 - (f-1) \int_0^{\infty} p(t) \rho(t) dt} \quad (19)$$

which by eq 12 is simply the familiar *batch* reactor result.¹⁵ Thus we see that it is not merely the residence time distribution that is the source of the nonideality, but rather that the residence time distribution forces non-random combination of monomers. That is, a monomer with a residence time t' does not combine with other monomers with a probability proportional to $p(t)$; rather, the residence time distribution of the first generation is different from the overall distribution. In fact, the expected residence time of a first generation monomer is $\theta(1 - (\tau/(\theta+\tau))^2)$, which is less than the value for the zeroth generation monomer, θ . The "skewing" of the residence time distribution will also occur for every successive generation, and so the nonideality may be called a long-range effect. The problem can nonetheless be

solved exactly, as shown below. (All results will be expressed in terms of the conversion p ; see eq 8).

I. The Case $f = 2$.

Under the initial condition $E(N_A^{\text{out}} | 0) = 0$, and the restriction that DP_w must be finite, eq 17 is easily solved to yield:

$$E(N_A^{\text{out}} | t) = \frac{\theta}{\tau} \left(\frac{1}{\tau} + \frac{1}{\theta} \right) t \quad (20)$$

The expected weight on a monomer thus grows *linearly* with residence time. Integrating according to eq 13, we find the weight-average degree of polymerization to be:

$$DP_w = \frac{1 + p^2}{(1 - p)^2} \quad (7)$$

as before.

II. The Case $f > 2$.

The solution of eq 17 depends upon whether we are operating below, above, or at the critical conversion p_c , or the corresponding critical Damköhler number, Da_c :

$$p_c = 1 - 2(f-2) \left(\sqrt{1 + \frac{1}{f-2}} - 1 \right) \quad (21)$$

$$Da_c = \frac{1}{4(f-2)} \quad (22)$$

as found from the discriminant of the characteristic equation. We will examine each case in turn.

A. $p \leq p_c$. With the initial condition that $E(N_A^{\text{out}} | 0) = 0$, and the condition that as p (or Da) approaches zero DP_w must approach unity, the solution is:

$$E(N_A^{\text{out}} | t) = \frac{1}{f-2} (e^{\lambda t} - 1) \quad (23)$$

where

$$\lambda = \frac{1}{2\theta} \left(1 - \sqrt{1 - 4(f-2) \frac{\theta}{\tau} \left(1 + \frac{\theta}{\tau} \right)} \right) \quad (24)$$

In contrast to the linear A_2 homopolymerization, for the nonlinear case the expected weight on a monomer grows *exponentially* with residence time. The weight-average degree of polymerization is given by:

$$DP_w = \frac{f}{(f-2)^2} \frac{1-p}{2p} \left((1-p) - \sqrt{(1-p)^2 - 4(f-2)p} \right) - \frac{2}{f-2} \quad (25)$$

in agreement with the solution which can be obtained from the kinetic equations (see Appendix).

B. $p=p_c$. Here we obtain:

$$E(N_A^{\text{out}} | t) = \frac{1}{f-2} (e^{1/2\theta} - 1) \quad (26)$$

which in turn gives DP_w as follows:

$$DP_w = 2 \frac{f-1}{f-2} \quad (27)$$

Thus the largest DP_w to be obtained is four, for $f=3$; as f approaches infinity, the largest DP_w goes to two.² Thus, despite the broad distributions, we do not obtain high polymer.³ (The polydispersity here is deceptively low, for at any Damköhler number all moments above a critical moment are divergent.⁶)

C. $p > p_c$ For this case, the roots of the characteristic equation are complex and thus the solution is of the form:

$$E(N_A^{out} | t) = e^{t/2\theta} \left\{ c_1 \sin\left(\frac{t}{2\theta} \sqrt{4(f-2) \frac{\theta}{\tau} \left(1 + \frac{\theta}{\tau}\right) - 1} \right) + c_2 \cos\left(\frac{t}{2\theta} \sqrt{4(f-2) \frac{\theta}{\tau} \left(1 + \frac{\theta}{\tau}\right) - 1} \right) \right\} - \frac{1}{f-2} \quad (28)$$

an equation which makes no physical sense, as it allows $E(N_A^{out} | t)$ to be negative. Indeed, DP_w is found to be given by eq 25, and thus itself to have an imaginary component. We thus conclude either that steady state operation is not possible for $p > p_c$,² or that the steady state is a gelling one.⁶ Practically, of course, gelation would make operation of an HCSTR impossible anyway, such that from an engineering viewpoint p_c gives the critical conversion (and hence Da_c) above which steady state operation is not possible.

DP_n .

The number-average degree of polymerization can always be calculated from simple stoichiometric reasoning, being related only to the number of reacted groups and not to the details of connectivity. Thus:

$$DP_n = \frac{1}{1 - (f/2)p} \quad (29)$$

in agreement with the result from the kinetic equations (see Appendix).

Discussion

For the sake of illustration, we examine the case $f=3$; all of the conclusions drawn, however, are independent of f . The steady state values of the number- and weight-average degrees of polymerization are shown in Figure 2, which emphasizes that high polymer is simply not obtained in a single HCSTR. However, while DP_w is finite (and in this case equal to four) at the critical conversion, it should be noted that (dDP_w/dp) is infinite. Insight can also be gained from comparison of the HCSTR results with those from a batch reactor;¹⁵ we can compare on the basis of either conversion or Damköhler number. For DP_w , Figures 3 and 4 show these comparisons; on either basis, the HCSTR product exhibits a higher DP_w than the batch reactor product, as expected. This is obviously not due to increased conversion at a given Da ; indeed, Figure 5 shows that the DP_n for the HCSTR product is lower than that from a batch reactor at the same Da , indicating a correspondingly lower conversion. (A comparison of DP_n on the basis of conversion is not shown, because there is no difference between the two on this basis.)

In conclusion, the recursive method has been extended to HCSTRs, proper care being taken to account for residence time distribution and the accompanying non-random reaction. The results obtained are in agreement with kinetic derivations, and although this derivation is not necessarily simpler or more powerful than the kinetic derivation (indeed, we have only solved the steady-state situation), it does offer insight into how the structure changes with residence time of the monomer. More importantly, it demonstrates the power of the statistical method to account, rigorously, for nonideality, in this case a violation of both the independent and equal reactivity assumptions enforced by the reactor configuration. While the ideas presented here could be extended to other more practical chemical systems (e.g. $A_f + B_2$) or to other types of reactors, perhaps they will find greater utility in the analysis of nonidealities intrinsic to the reaction chemistry.

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Appendix: Derivation of DP_w and DP_n from kinetic equations for $f > 2$.

The kinetic equation describing the polymerization is essentially Smoluchowski's coagulation equation with source and sink terms,⁶ and with a kernel appropriate to A_f homopolymerization:¹⁶

$$\frac{dc_n}{dt} + \frac{c_n - c_{n0}}{\theta} = \frac{k}{2} \sum_{i+j=n} [(f-2)i+2][(f-2)j+2]c_i c_j - k [(f-2)n+2] c_n \sum_{i=1}^{\infty} [(f-2)i+2]c_i \quad (A1)$$

where c_{n0} is the entering n -mer concentration. The first three moments, μ_i ($i=0,1,2$), of the distribution evolve according to the following expressions:¹⁷

$$\frac{d\mu_0}{dt} + \frac{\mu_0 - \mu_{00}}{\theta} = -k \left\{ (1/2)(f-2)^2 \mu_1^2 + 2(f-2)\mu_1 \mu_0 + 2\mu_0^2 \right\} \quad (A2)$$

$$\frac{d\mu_1}{dt} + \frac{\mu_1 - \mu_{10}}{\theta} = 0 \quad (A3)$$

$$\frac{d\mu_2}{dt} + \frac{\mu_2 - \mu_{20}}{\theta} = k \left\{ (f-2)^2 \mu_1^2 + 2(f-2)\mu_2 \mu_1 + 4\mu_1^2 \right\} \quad (A4)$$

where μ_{i0} is the entering i^{th} moment. The concentration of unreacted functional groups $[A]$ (which equals $\{(f-2)\mu_1 + 2\mu_0\}$) obeys the following equation:

$$\frac{d[A]}{dt} + \frac{[A]-[A]_0}{\theta} = -k[A]^2 \quad (A5)$$

For steady-state operation (i.e. the time derivatives vanish) and only monomer entering ($\mu_{00}=\mu_{10}=\mu_{20}=c_{10}$), solution of the above (algebraic) equations gives:

$$\mu_0 = \left(1 - \frac{f}{2} \left(1 - \frac{\sqrt{1+4Da} - 1}{2Da} \right) \right) c_{10} \quad (A6)$$

$$\mu_1 = c_{10} \quad (A7)$$

$$\mu_2 = \left(\frac{f\sqrt{1-4(f-2)Da}}{2Da(f-2)^2} - \frac{2}{f-2} \right) c_{10} \quad (A8)$$

From eq A5, the conversion is found to be given by eq 8, and upon defining $DP_w=\mu_2/\mu_1$ and $DP_n=\mu_1/\mu_0$, eqs 25 and 29 are obtained.

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- (12) Extension to multistage batch processes is, of course, possible; see, for example:
- (a) Dusek, K.; Scholtens, B. J. R.; Tiemersma-Thoone, G. P. J. M. *Polym. Bull.* 1987, 17, 239; Scholtens, B. J. R.; Tiemersma-Thoone, T. P. J. M. *Polym. Mat. Sci. Eng.* 1988, 58, 262. (b) Miller, D. R. "Calculation of Network Parameters of Crosslinked Markovian Polymer Chains," presented at Networks '88, the 9th Polymer Networks Group Meeting, Freiburg, West Germany, September 26-30, 1988.
- (13) A semi-batch step polymerization of the kind $A_f + B_2$, where all B_2 molecules are initially present in the reaction bath, has been analyzed by recursive techniques using the concept of "superspecies"; Galván, R., manuscript in preparation. For a discussion of superspecies see Miller, D. R.; Macosko, C. W. in *Biological and Synthetic Polymer Networks*; Kramer, O., Ed.; Elsevier Applied Science, London, 1988.
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- (17) The equation for μ_2 is valid even though μ_3 may be infinite (which is the case at steady state for $Da \geq (8/9)Da_c$)²; Ziff, R. M., personal communication.

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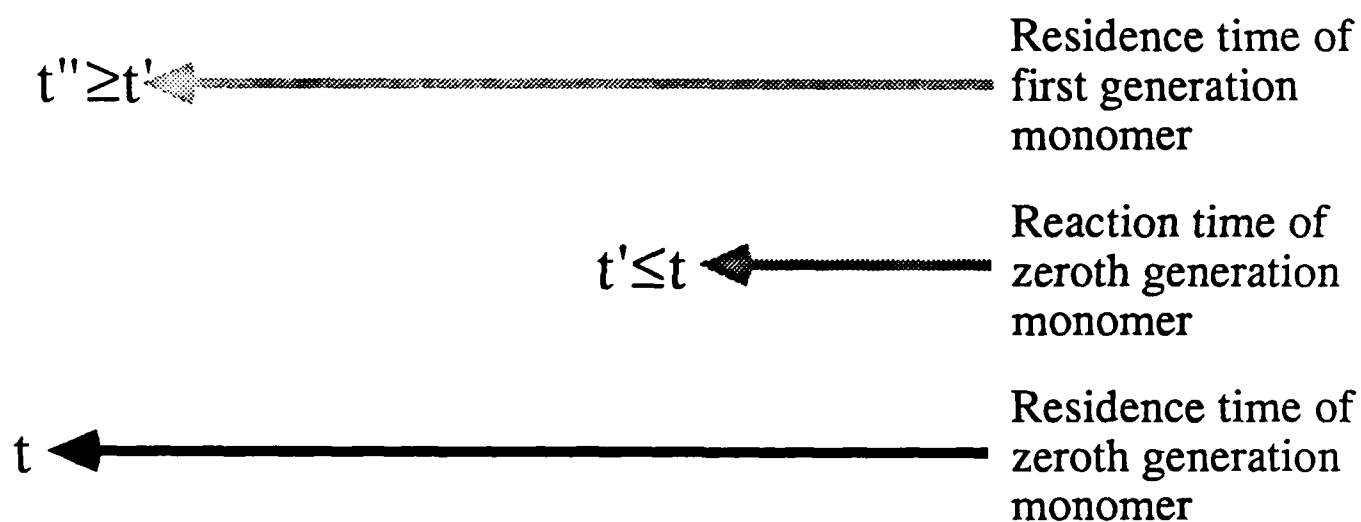


Figure 1

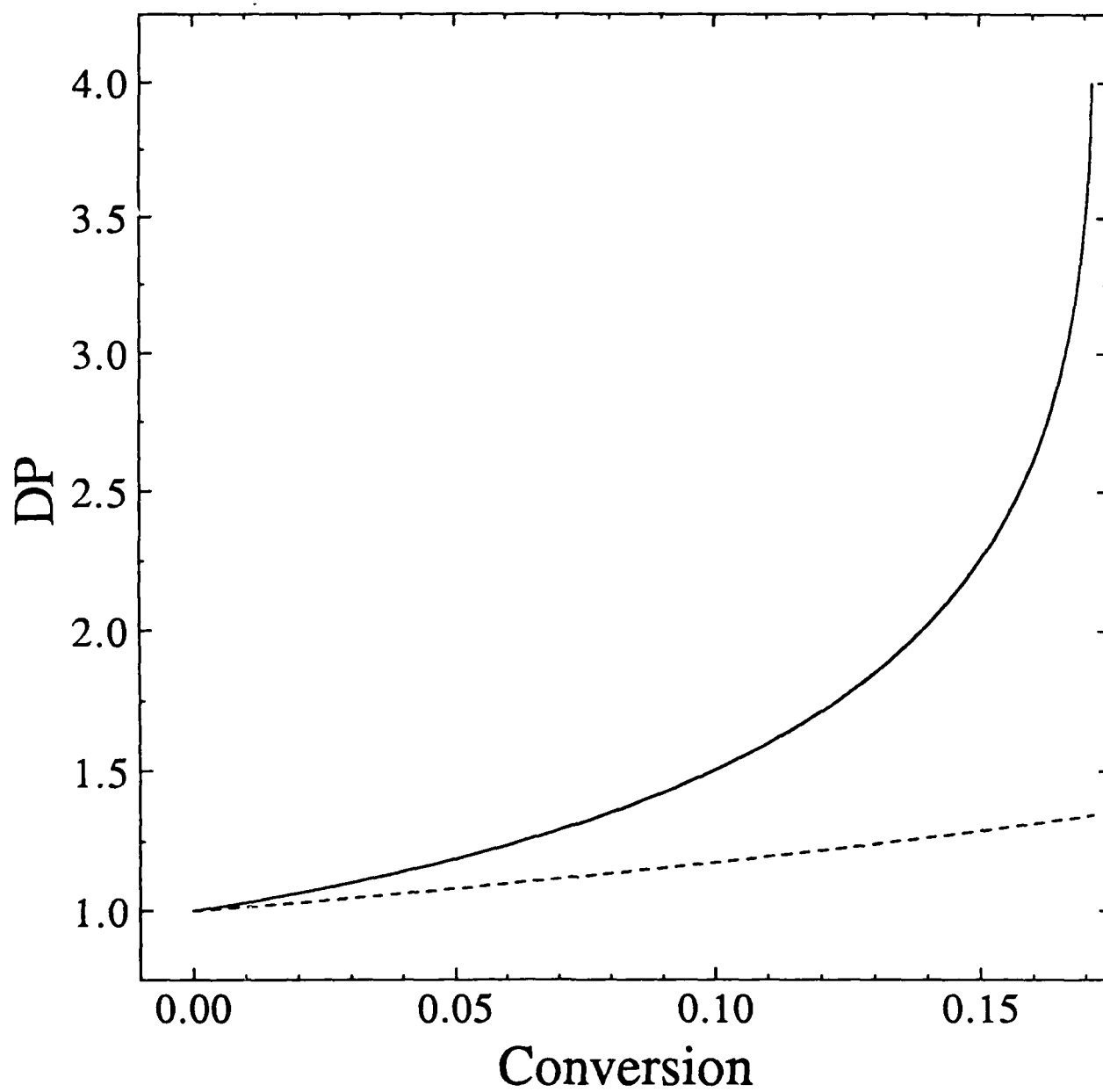
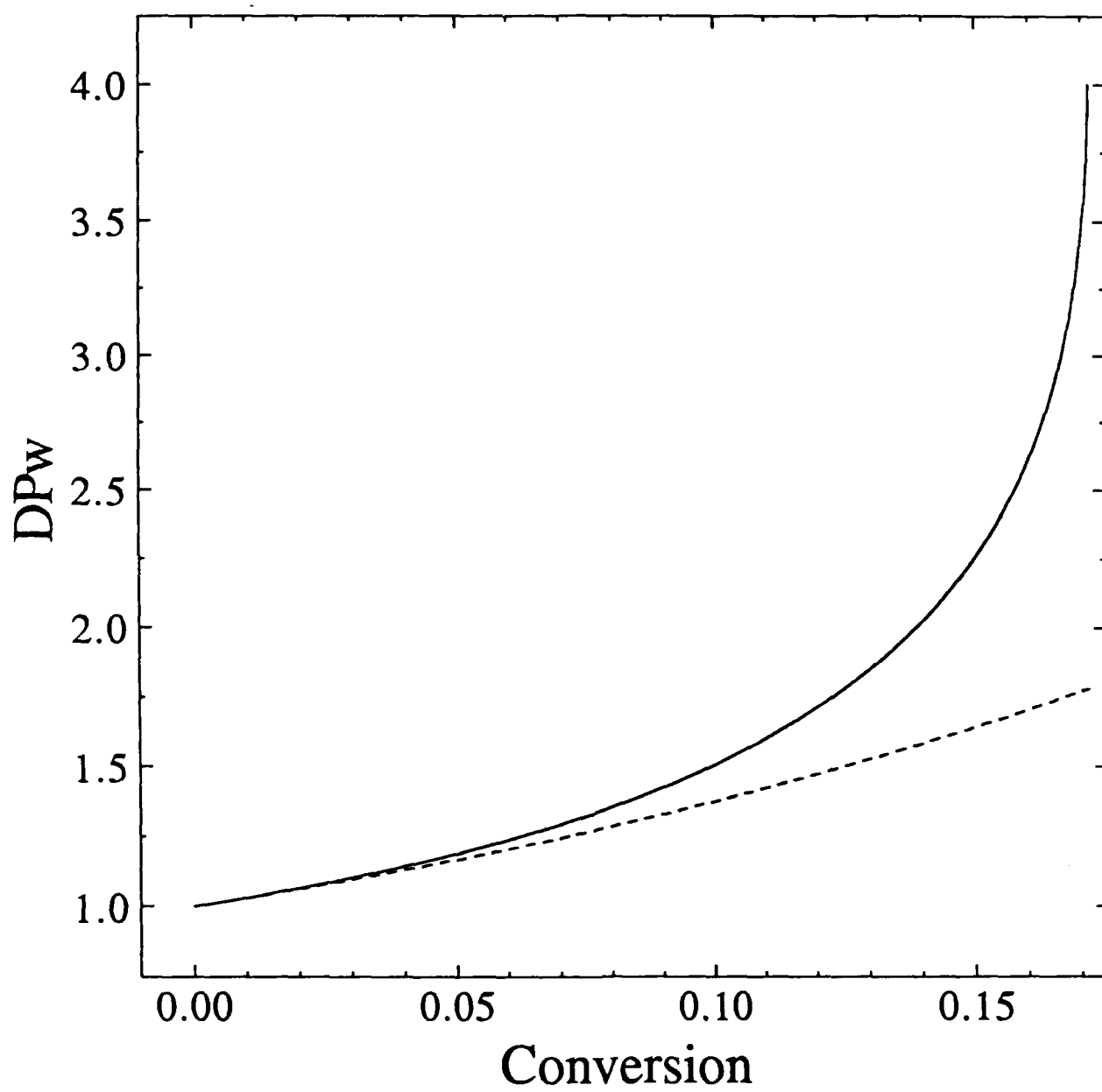
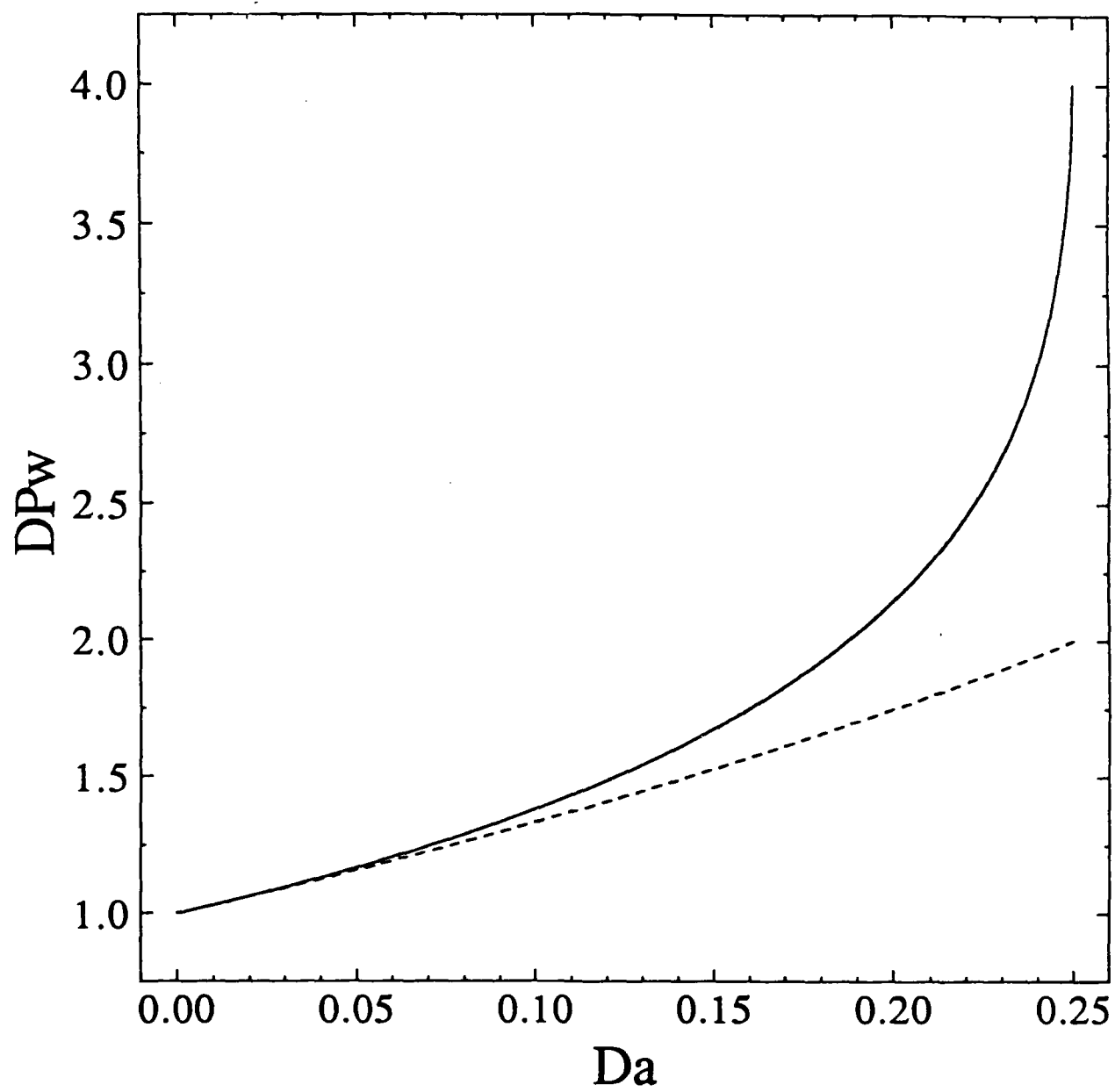


Figure 2





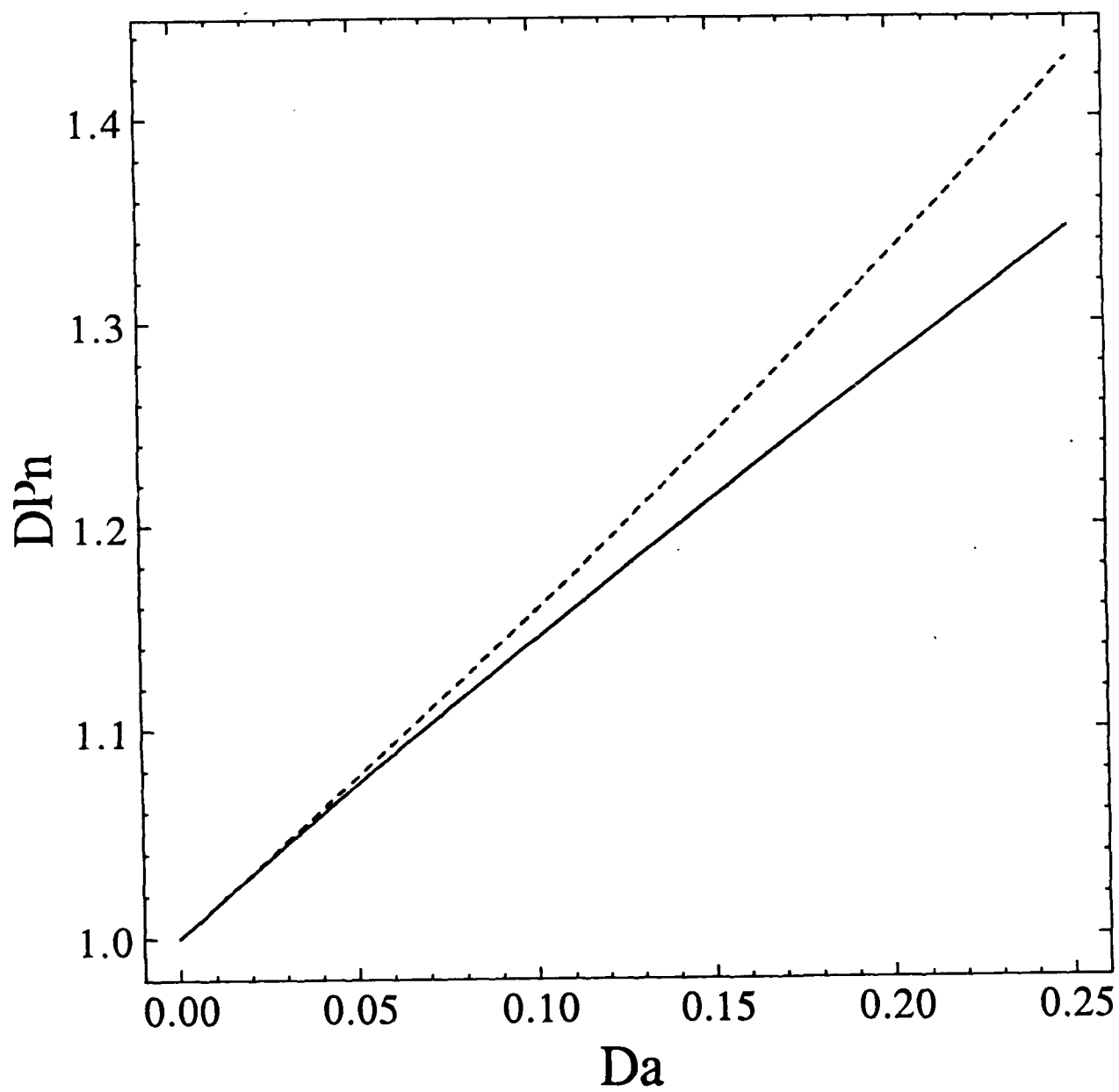


Figure 5